

2. The method of claim 1, wherein the at least one sample comprises at least one protein solution.

3. The method of claim 1, wherein the at least one sample comprises at least one population of cells.

4. The method of claim 3, wherein the at least one population of cells is incubated in a fixing and rinsing agent prior to the step of spraying the substrate with an enzymatic releasing solution.

5. The method of claim 4, wherein the fixing and rinsing agent is selected from the group consisting of: formalin, Carnoy's solution, paraformaldehyde, an ethanol-based fixative, and a polyethylene glycol-based fixative.

6. The method of claim 1, wherein the substrate is a glass or plastic microscope slide or multiwell plate.

7. The method of claim 1, wherein the blocking solution is a serum.

8. The method of claim 7, wherein the serum is 1% BSA in PBS and detergent.

9. The method of claim 1, wherein the blocking solution is removed with a wash step comprising 3×PBS baths and 1× water bath.

10. The method of claim 1, wherein the at least one sample is incubated in a humidity chamber at room temperature for two hours.

11. The method of claim 1, wherein the enzymatic releasing solution comprises PNGase F.

12. The method of claim 1, wherein the mass spectrometry is selected from the group consisting of: matrix-assisted laser desorption/ionization imaging Fourier transform ion cyclotron resonance (MALDI-FTICR) mass spectrometry, matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry, scanning microprobe MALDI (SMALDI) mass spectrometry, infrared matrix assisted laser desorption/ionization (MALDI-ESI) mass spectrometry, surface-assisted laser desorption/ionization (SALDI) mass spectrometry, desorption electrospray ionization (DESI) mass spectrometry, secondary ion mass spectrometry (SIMS) mass spectrometry, and easy ambient sonic spray ionization (EASI) mass spectrometry.

13. The method of claim 12, wherein the scanning step is preceded by a step of spraying the substrate with a MALDI matrix material.

14. The method of claim 13, wherein the MALDI matrix solution is selected from the group consisting of: 2,5-dihydroxybenzoic acid,  $\alpha$ -cyano-4-hydroxycinnamic acid, sinapinic acid, 1,5-diaminonaphthalene, and 9-aminoacridine.

15. The method of claim 1, wherein the plurality of antibodies specifically bind to a protein selected from the group consisting of: A1AT, fetuin-A, hemopexin, Apo-J, LMW Kininogen, HMW Kininogen, apo-H, transferrin, IgG, IgM, IgA, fibronectin, laminin, ceruloplasmin, fibulin, angiotensinogen, Fibrillin-1, TIMP1, thrombospondin 1, galectin-3 binding protein, complement C1 R, clusterin, galectin 1, alpha-2-macroglobulin, Vitamin D binding protein, histidine rich glycoprotein, histidine rich glycoprotein, CD109, CEA, Cathepsin, AFP, GP731, and combinations thereof.

16. The method of claim 14, wherein the antibodies are useful in detecting the presence of hepatocellular carcinoma.

17. A method for glycan analysis of at least one population of cells, the method comprising the steps of:

adhering at least one population of cells to a surface of a substrate;

fixing and rinsing the at least one population of cells; spraying the substrate with an enzymatic releasing solution; and

scanning the substrate by mass spectrometry to detect and identify the presence of glycans.

18. The method of claim 17, wherein the at least one population of cells is adhered by culturing, deposition, swabbing, smearing, or centrifugation.

19. The method of claim 17, wherein the fixing and rinsing agent is selected from the group consisting of: formalin, Carnoy's solution, paraformaldehyde, an ethanol-based fixative, and a polyethylene glycol-based fixative.

20. The method of claim 17, wherein the substrate is a glass or plastic microscope slide or multiwell plate.

21. The method of claim 17, wherein the substrate surface includes one or more of: an indium tin oxide coating, a gelatin coating, a collagen coating, a poly-L-lysine coating, a poly-ornithine coating, an extracellular matrix coating, a protein coating, and surface ionization.

22. The method of claim 17, wherein the enzymatic releasing solution comprises PNGase F.

23. The method of claim 17, wherein the mass spectrometry is selected from the group consisting of: matrix-assisted laser desorption/ionization imaging Fourier transform ion cyclotron resonance (MALDI-FTICR) mass spectrometry, matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry, scanning microprobe MALDI (SMALDI) mass spectrometry, infrared matrix assisted laser desorption/ionization (MALDI-ESI) mass spectrometry, surface-assisted laser desorption/ionization (SALDI) mass spectrometry, desorption electrospray ionization (DESI) mass spectrometry, secondary ion mass spectrometry (SIMS) mass spectrometry, and easy ambient sonic spray ionization (EASI) mass spectrometry.

24. The method of claim 23, wherein the scanning step is preceded by a step of spraying the substrate with a MALDI matrix material.

25. The method of claim 24, wherein the MALDI matrix solution is selected from the group consisting of: 2,5-dihydroxybenzoic acid,  $\alpha$ -cyano-4-hydroxycinnamic acid, sinapinic acid, 1,5-diaminonaphthalene, and 9-aminoacridine.

26. A kit for glycan analysis of protein samples, comprising:

at least one substrate, each substrate having a surface spotted with a plurality of antibodies;

at least one blocking solution;

at least one enzymatic releasing solution; and

at least one MALDI matrix material.

27. The kit of claim 24, wherein the substrate is a glass or plastic microscope slide or multiwell plate.

28. The kit of claim 24, wherein the blocking solution is a serum.

29. The kit of claim 24, wherein the serum is 1% BSA in PBS and detergent.

30. The kit of claim 24, wherein the enzymatic releasing solution comprises PNGase F.

31. The kit of claim 24, wherein the MALDI matrix solution is  $\alpha$ -cyano-4-hydroxycinnamic acid.

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